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A STUDY ON THE PRECIPITATION OF CALCIUM AS CALCIUM FLUORIDE

A Dissertation

Submitted to the Graduate Faculty of the
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in partial fulfillment of the
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in

The Department of Chemistry

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Raul Morales
B.S., University of Southwestern Louisiana, 1961
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ABSTRACT

A procedure for the gravimetric determination and precipitation of calcium as calcium fluoride by the homogeneous generation of fluoride ions in the solution is presented. The method described produces a precipitate which is crystalline and easily filtered as contrasted to the usual slimy, colloidal and difficultly filtered calcium fluoride obtained by conventional procedures.

The precipitation is effected from homogeneous solution by kinetically controlling the formation of the precipitant, the fluoride ion. Such a mechanism results when a solution containing calcium, ammonium chloride, urea and fluoboric acid is heated to the point of boiling. The urea hydrolyzes which in turn facilitates the hydrolysis of the fluoborate anion and effects the subsequent precipitation of the calcium, i.e.,

1) $CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$

2) $BF_4^- + H_2O = BF_3(OH)^- + HF$

3) $2HF + Ca^{++} = CaF_2 + 2H^+$

The effect of certain interferences and factors affecting the characteristics of the precipitate as well as the completeness

of precipitation are discussed. The recommended procedure yields quantitative results and also presents a means for an easier and more effective separation of barium from calcium when the latter is determined gravimetrically.

CHAPTER I

INTRODUCTION

Calcium is a member of the group IIA elements of the Periodic Table, associated with beryllium, magnesium, strontium, barium and the radioactive radium. It is one of the "alkaline earths," this name originating in the early annals of chemistry when all non-metallic substances which were insoluble in water and unaffected by fire were called "earths". Both lime and magnesia (the oxides of calcium and magnesium respectively) exhibited an alkaline reaction and consequently were called "alkaline earths" (28).

Although the Romans prepared lime in the first century, it was not until 1808 that calcium was discovered by Davy when he isolated it by electrolysis. Davy was able to separate the metal in this manner by considering Lavoisier's suggestion that the alkaline earths were oxides and should be treated as such.

Calcium is a metallic element, comprising 3.4% (by weight) of the earth's crust thus making it the fifth most abundant element in the crust. In sea water it is found in

amounts of 400g/ton. Because it is a rather reactive metal, it is never found uncombined in nature. It occurs abundantly as limestone and marble ($CaCO_3$), apatite $[Ca_5(Cl,F)(PO_4)_3]$, gypsum ($CaSO_4.2H_20$), fluorite (CaF_2), and also together with silicates in rocks, etc. The concentration of calcium in fresh waters is variable since the solubility of calcium will be dependent upon its chemical form in the different rocks and soils that are in contact with the water. Its concentration in fresh water may vary from less than 10 parts per million to 30-100 parts per million. The latter concentrations may apply, for example, to those waters which come in contact with limestone formations; the former, to those associated with granitic rocks or silicious sand. Waters which percolate through gypsiferous shale may contain calcium in concentrations as high as several hundred parts per million (33).

In the last thirty or forty years calcium has shown a consistent growth in usage and importance. It is not a bulk product in itself, but comparatively small amounts have a great effect on the properties of the materials to which it is added. For example, in the field of metallurgy calcium is used as a reducing agent in preparing other metals such

as uranium, zirconium and thorium. It is also used as a desulfurizer, decarbonizer or deoxidizer for various alloys of iron, copper, beryllium, etc. Lead used in bearings can be hardened by adding calcium, and flints for cigarette and gas lighters may contain cerium alloyed with this group IIA element. Electronic companies use the metal as a "getter" to fix residual gases as oxides, nitrides and hydrides of calcium. Calcium compounds are also important in industry. Natural and synthetic rubbers show an increased resistance towards tearing, stiffness, and hardness when inorganic pigments of calcium carbonate and calcium silicate are added to them (8). Calcium sulfate is used as a fertilizer to restore the soil's sulfur removed by growing plants. Although not generally realized by many people, calcium hydroxide is as strong a base as sodium hydroxide. Due to its more limited solubility, however, it does not form a concentrated solution.

The oxide of calcium is used to make mortar and plaster and to raise the pH of acidic soils. Other properties and uses of calcium salts are generally well known. In the presence of sulfate or alkaline substances, calcium can cause boiler scale. A favorable ratio of calcium to sodium is

desirable in irrigation water because it flocculates soil colloids and therefore improves porosity. Along with magnesium and iron, calcium salts are responsible for "hard" water.

Physiologically, calcium is of extreme importance. For example, it activates the enzyme myosin adenosine triphosphatase, whose function in the body is believed to lead to the immediate source of chemical energy for muscular contraction (31). The enzymic hydrolysis of organic phosphatases in the presence of calcium ions is generally believed to cause the deposition of calcium phosphate in the bones of growing animals. Calcium in the bones of animals occurs as carbonate, phosphate, and to some extent as fluoride. The skeletal material of invertebrates is primarily based on calcium carbonate whereas that of vertebrates is mainly in the form of phosphate. One of the reactions involved in blood coagulation--the conversion of prothrombin to thrombin--requires the presence of calcium ions. Studies have shown that cows with high milk production have a positive calcium balance and those with low milk production have a negative one. Kraut and Wecker have studied the calcium balance and requirements for the human organism and stated

that 0.5g calcium in the daily diet generally is sufficient to compensate for the temporary tendencies that the organism shows with respect to either the retention or loss of calcium (24).

The uses and properties of calcium and its salts as described above, serve to illustrate that the analysis of calcium is of great importance whether we are considering a water, soil or tissue sample. There are various ways in which calcium may be determined ranging from the very sophisticated method of neutron activation analysis to the old classical method of gravimetry. With respect to the latter, the most satisfactory precipitation of calcium is as the oxalate; all other precipitations having various undesirable characteristics. An additional good gravimetric method for calcium is, therefore, of practical and academic interest when dealing with quantities in the macro and semi-micro scale. With this in mind, the precipitation of calcium as the fluoride was considered.

The precipitation of calcium oxalate is never quite complete and the first precipitate is seldom pure, its usual contaminants being the alkali metals, magnesium, barium and strontium. Barium cannot be tolerated, and if present even

in milligram amounts, will require that the calcium oxalate precipitate be reprecipitated two or three times in order to separate the two elements. [The solubility product for $BaC_2O_4.3\frac{1}{2}H_2O$ is $1.62 \times 10^{-7}(18^{\circ})$ and for $CaC_2O_4.H_2O$ is $1.78 \times 10^{-9}(18^{\circ})$] Fluoride also interferes when calcium oxalate is precipitated by combining with the metal to form calcium fluoride.

Some of the more common weighing forms of calcium which have been proposed are: $CaC_2O_4.H_2O$, CaC_2O_4, $CaCO_3$, CaO, $CaSO_4$, and CaF_2. The first four forms are obtained by heating the calcium oxalate precipitate at certain temperatures, and the last two by treating the precipitate, or its ignition products, with sulfuric or hydrofluoric acids respectively. The monohydrated precipitate is undesirable because it contains trapped water which is not expelled at the recommended heating temperatures, is hygroscopic, and can easily decompose while heating. Calcium carbonate is a more suitable weighing form but the heating temperatures have to be strictly controlled, otherwise, dissociation of the precipitate takes place. Calcium oxalate and calcium oxide are both very hygroscopic and the latter has the added disadvantages of absorbing carbon dioxide and having a low molecular

weight. The treatment of any of these weighing forms with sulfuric acid to convert them to calcium sulfate, usually leads to loss by spattering.

Calcium fluoride is a desirable weighing form for calcium because:

(a) it is not hygroscopic

(b) its heating temperature does not have to be rigidly controlled and

(c) its molecular weight is reasonable.

Precipitation of calcium as the fluoride has the added advantages that presence of fluoride ions will not interfere in the analysis and it does not have to be converted into another form for weighing. Furthermore, this precipitate offers a possibility for a better and easier separation of calcium from barium since the respective solubility products of their fluorides are $3.95 \times 10^{-11}(26^{o})$ and $1.73 \times 10^{-6}(25.8^{o})$. Because precipitation from homogeneous solution usually leads to a more dense and easily filterable precipitate as well as one having minimal coprecipitation and because of the already mentioned desirable traits of calcium fluoride, it seemed possible that the precipitation of calcium fluoride from homogenous solution might provide

a means for effecting a reliable gravimetric procedure for a quantitative determination of calcium.

CHAPTER II

PRECIPITATION

A. INTRODUCTION

Gravimetric analysis deals with the preparation and weighing of a stable substance whose composition is known and contains the constituents to be determined. The usual way of doing this is to cause the stable substance to precipitate from a solution, leaving behind materials which might interfere with the composition of the substance. Gravimetric analysis is generally considered a difficult technique and is quite often avoided on the grounds of being time-comsuming. However, this method of analysis, although replaced largely by instrumentation in routine work, has retained its value as a method of ultimate reference. For the standardization of samples, uncertainties are reduced or eliminated. Despite its greater demands on technical skill and time, compensation is obtained in the assurance of an isolated compound and in the accuracy associated with a weighing form whose purity can easily be ascertained.

Precipitation is one of the oldest chemical techniques which has been employed by the analytical chemist. Qualitative analysis depends largely on precipitate formation and its subsequent identification. If the precipitate is dissolved and titrated, then it serves as a basis for a titrimetric method. Instrumental methods frequently depend on a precipitation step for separation from interferences or for concentration of some element initially present at such dilution as to be below the sensitivity of the instrument. Indeed, there are relatively few analytical methods which do not have a precipitation step at some point in their procedure.

B. THEORY

The theory and mechanisms involved in precipitation are quite complex. "Nucleation" is defined by La Mer as "the process of generating within a metastable mother phase the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase" (26). The mechanisms of nucleation affect the nature and purity of the resulting precipitates. If the precipitation is effected in such a way that numerous nuclei are

produced, then precipitation will be rapid, individual crystals very small, filtration and washing difficult and purity low. But if the precipitation is effected so as to produce only a few nuclei, then the precipitation will be slower, crystals larger, filtration and washing easier and purity higher. It is evident, therefore, that control of the nucleation processes is of considerable importance in gravimetric work.

The manner in which nuclei are created is not definitely known. The study of the energetics and kinetics for such a process is a challenging task. From the point of view of energetics, however, consider a substance being transformed from one phase into another such as takes place in precipitation from a solution (32). The change in the Gibbs free energy, G, at constant temperature and pressure may be written

$$\Delta G = (\mu_2 - \mu_1)\,\Delta n \qquad (2.1)$$

where n represents the amount of substance transformed from the phase where its chemical potential is μ_1 to a phase of potential μ_2. The intensive quantity which measures the driving force of the phase change is defined as

$$\varnothing = -\Delta G/\Delta n = \mu_1 - \mu_2 \qquad (2.2)$$

When $\phi > 0$ the transition from 1 to 2 is a natural, spontaneous process. When $\phi < 0$ the transition is improbable; $\phi = 0$ is a necessary and sufficient condition for equilibrium with respect to the transition.

In the case of small portions of matter--such as the nuclei of a recently manifested phase--it is important that the molecules or ions in the surface layer are in a higher potential energy state than are the interior molecules or ions. Because this excess energy is not compensated by a sufficient excess of entropy, the free energy of the molecules forming at the particle's surface is greater than that anywhere else.

For bodies of macroscopic dimensions, this excess free energy can be expressed by the surface tension, σ, which is the surface free energy per unit area of surface. But for nuclei composed of a small number of ions or molecules (e.g., 10-100), the definition of surface area is rather ambiguous, and probably the surface tension will depend on the size regardless of how it is defined geometrically.

For the sake of convenience, however, the usual concepts of surface and surface tension are retained. The surface tension of solids has been measured in only a few cases and

never very accurately. Surface tensions of some ionic crystals in a vaccum may be calculated with five per cent uncertainty in some cases but the needed values for crystals in solution have not been determined. If it is assumed that all small crystals of a substance are similar, then one can set the area, A, proportional to $n^{2/3}$, n being the number of molecules or ions in the crystals. With this assumption the following expression for the free energy change in forming a crystal from homogeneous solution is obtained:

$$\Delta G = -n\phi + \sigma A = n\phi + n^{2/3}\psi \qquad (2.3)$$

where both ϕ and ψ are independent of n. Only positive values of ψ need be considered. (Notice that ψ is a coefficient relating surface free energy to the number of ions or molecules in a crystal).

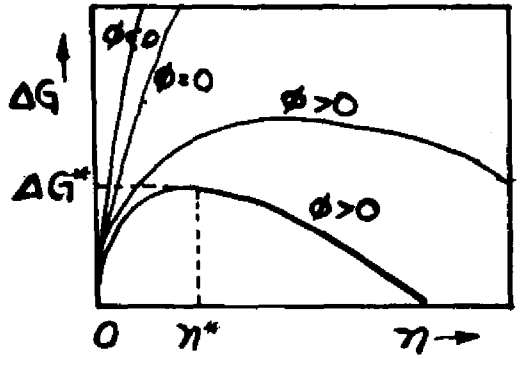


Fig. 2.1 Free energy of formation for a crystal or a droplet consisting of n molecules or ions. ϕ is the affinity per molecule for the phase transition when surface phenomena are neglected (32).

Figure 2.1 shows that ΔG is positive for all values of n when $\phi < 0$. In a supersaturated solution, however, ΔG is negative for sufficiently large n-values because n goes to infinity faster than $n^{2/3}$. For n values close to zero, ΔG is always positive. The maximum change in free energy is found by letting $d\Delta G/dn = 0$,

$$n = n^* = (2\Psi/3\phi)^3 \tag{2.4}$$

Because the free energy does not vary for an infinitesimal change of n when $n = n^*$ this is, a state of equilibrium. But it follows from

$$\left[d^2\Delta G/dn^2\right]_{n' = n^*} < 0 \tag{2.5}$$

that when the system is shifted slightly from equilibrium, no matter how little, it has no tendency to go back to it again, i.e., the equilibrium is unstable. Particles with $n > n^*$ will grow without limit but particles smaller than n^* dissolve completely.

Thermodynamically speaking, a homogeneous, supersaturated solution is in a stable (or metastable) condition and will remain so indefinitely. Although a free energy barrier has to be overcome, crystallization is believed to start because of statistical fluctuations in the free energy in small parts of the system.

Therefore, in order to initiate nucleation, it is necessary that the solution be supersaturated, i.e., contain a greater quantity of dissolved substance than is predicted by its solubility product. An increase in supersaturation causes a corresponding increase in the probability of nucleation. The degree of supersaturation is expressed by the supersaturation ratio, defined as the square root of the ion activity products in the supersaturated state to those in the saturated state,

$$S.R. = (K_{ss}/K_{sp})^{1/2} \qquad (2.6)$$

The solutions are rather stable when the supersaturation ratio is very small since only a few nuclei are formed. Precipitation in such cases may take place in several days or months. Spontaneous formation of the precipitate results when the critical supersaturation ratio is reached. This critical point is not a fixed constant but varies with such factors as impurities in the solution, cleanliness of the vessel, temperature and solubility, etc.

There are several good treatments of nucleation in theory and practice two of which are the fine works of Nielsen (32) and Walton (40). The chapter on precipitation in the book by Berg (2) also presents aspects of the nucleation theory in

a more compact form.

Once nucleation has been initiated, crystal growth proceeds until supersaturation of the precipitating material is eliminated, i.e., until an equilibrium solubility is attained. Generally, upon digestion with the mother liquor the larger crystals grow at the expense of smaller ones because the smaller crystals have a greater solubility. This phenomenom, known as Ostwald ripening, leads to a solution supersaturated with respect to the larger crystals.

Preceding the development of the present nucleation and crystal growth theory, von Weimarn (37) related the effect of supersaturation on solute solubility. His mathematical formulation indicates that the velocity of precipitation is proportional to the solute concentration and its equilibrium solubility

$$V = k\left(\frac{Q-S}{S}\right) \qquad (2.7)$$

where

V = velocity of precipitation

Q = total concentration of substance in solution

S = equilibrium solubility of coarse crystals

Q - S = supersaturation at the moment of precipitation

(Q-S)/S = degree of supersaturation

k = proportionality constant

Equation (2.7) suggests that precipitation can be slowed down by increasing the solubility of the precipitate or by decreasing the concentration of the reactants. Recognition of the latter factor has been instrumental in the development of the technique known as precipitation from homogeneous solution (PFHS).

C. PRECIPITATION FROM HOMOGENEOUS SOLUTION

The slow addition of a precipitant, however, carefully regulated, introduces areas of heterogeneity and therefore relatively high concentrations of reagent. This method of approach encourages the formation of a large number of centers of crystallization. With the technique of precipitation from homogeneous solution, the precipitation is kinetically controlled through the generation of the precipitating agent by a homogeneous chemical reaction within the solution. Thus PFHS encourages the formation of few nuclei and eliminates the undesirable concentration effects which are always present in a conventional precipitation process. The resulting precipitate is dense, easily filtered and washed, and more often than not, exhibits minimal coprecipitation. This

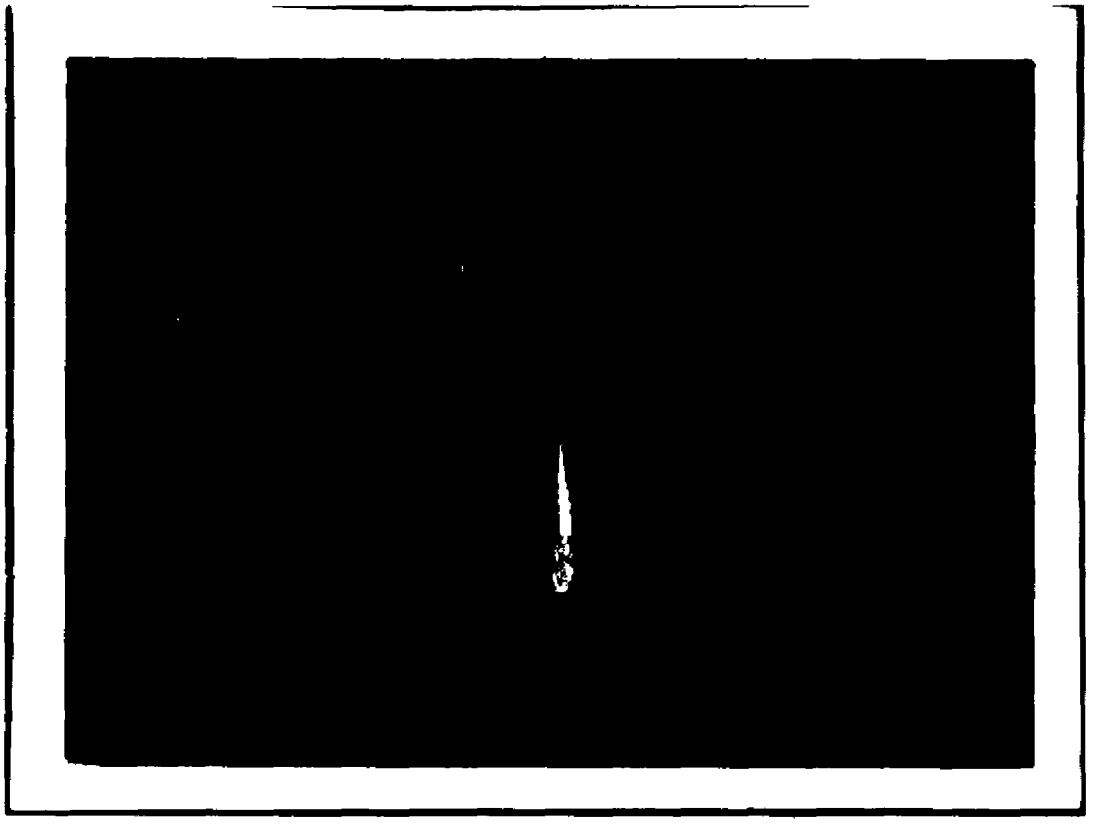


Fig. 2.2. Apparent volumes of calcium fluoride precipitated by the conventional method and from homogeneous solution.

last factor and PFHS as a whole, constitute landmarks in the progress of gravimetric analysis. The pronounced differences in the physical appearance of the precipitate formed by two different procedures is shown in Figure 2.2 and it is clear that the homogeneous method yields a more desirable precipitate.

Probably the biggest problem associated with precipitation processes is that of coprecipitation. This term may be broadly defined as the precipitation of a compound simultaneously with one or more other compounds. There are various types of coprecipitation and it is not always easy to differentiate among them. However, they may be tentatively classified according to the following mechanisms: mixed crystal formation, surface adsorption, and mechanical occlusion and inclusion. Surface adsorption is the most common mechanism by which coprecipitation takes place.

Mixed crystal formation may be subdivided into two parts. If the coprecipitated compounds show continuous miscibility with one another then <u>isomorphous mixed crystals</u> are formed, and only one solid phase will be indicated by one set of x-ray diffraction patterns. On the other hand, those compounds of dissimilar crystallographic types which exhibit a

lower miscibility form anomalous mixed crystals.

Adsorption on the surface of a precipitate after it has been formed is significant where a large surface area exists as is the case with flocculated colloids. Hahn (18) attributes the difference between an adsorption process and mixed crystal formation as that resulting from the effect of external conditions on the coprecipitation pattern of the trace constituent. With adsorption, the extent of coprecipitation depends on rate of precipitation, presence of other ions, crystal size, and other factors. With mixed crystal formation, the degree of coprecipitation is less dependent on the conditions of precipitation.

The trapping of an impurity within a precipitate as the subsequent layers are deposited gives rise to occlusion. If the trapped impurities are solvent molecules, then the term inclusion is used. If liquid inclusions are present, the crystal may decrepitate upon heating due to the ensuing internal pressure.

Postprecipitation refers to the phenomenom observed when two or more solid phases precipitate in a consecutive manner with a varying time interval between the formation of the various phases. This mode of precipitate contamination is

not considered to be an example of coprecipitation. However, it should be borne in mind that the initial phase which separates from solution undoubtedly carries with it by anomalous mixed crystal formation some of the subsequently appearing phase. Therefore, at least two mechanisms are involved.

The coprecipitation of impuritites with a precipitate is made easier by the presence of disorder and defects in the crystal structure except in cases where isomorphous replacement is involved. Large, well formed crystals generally are less contaminated than small imperfect crystals. Hence, coprecipitation of an impurity by adsorption and occlusion is largely eliminated when the technique of precipitation from homogeneous solution is utilized. Moreover, the coprecipitation data is usually more precise than that obtained by the direct addition of the precipitant because the precipitation conditions are more reproducible. The degree of local supersaturation which results by the addition of a precipitating agent in the conventional method is so erratic that it makes difficult a quantitative study of the impurity distribution in the solid and liquid phases.

A full mathematical treatment for the prediction of the extent of coprecipitation has not yet been formulated as can

well be imagined. The complex variables involved do not lend themselves readily for such a treatment. Nevertheless, there are two distributions laws which furnish a great deal of information on the subject.

The homogeneous distribution law predicts the distribution of impurities between the solid and liquid phases when the conditions are such that the precipitate is produced by conventional means, is digested sufficiently long to remove all concentration gradients and is homogeneous. Such conditions are, of course, seldom encountered in analytical work since in most precipitation reactions the rate of crystal growth is too rapid for the coprecipitated material to establish and maintain an equilibrium with the dissolved impurity. However, assuming that these conditions are present, then for a system in which substance A is precipitated in the presence of impurity B, the reaction is

$$A_{crystal} + B_{aq.} = A_{aq.} + B_{crystal} \qquad (2.8)$$

The equilibrium constant, D, is defined as

$$D = \frac{[A_{aq}][B_{crystal}]}{[B_{aq}][A_{crystal}]} \qquad (2.9)$$

which upon rearrangement gives the homogeneous distribution law,

$$(B/A)_{\text{entire crystal}} = D(B/A)_{\text{solution}} \qquad (2.10)$$

This distribution law has been used extensively by Henderson and Kracek (19), Wahl and Bonner (38) and others to express the distribution of radium between precipitated barium salts and their saturated solutions,

$$D = \frac{(Ra/Ba)\text{crystal}}{(Ra/Ba)\text{solution}} \qquad (2.11)$$

If, however, each crystal layer as it forms is in equilibrium with the solution existing at that time, then the logarithmic distribution law applies. This law of Doerner and Hoskins rewrites eq. (2.10) as

$$(B/A)_{\text{surface crystal}} = \lambda\,(B/A)_{\text{solution}} \qquad (2.12)$$

If dB and dA, the increments of foreign ions and precipitated substance deposited in the crystal layer, are proportional to their respective solution concentrations, then

$$\frac{dB}{dA} = \frac{\lambda(B_o - B)/V}{(A_o - A)/V} \qquad (2.13)$$

where B_o and A_o represent initial quantities in solution, B and A represent the quantities deposited in the crystal, and V is the volume of the liquid phase.

Equation (2.13) upon integration yields

$$\log B_o/B_f = \lambda \log A_o/A_f \qquad (2.14)$$

the logarithmic distribution law, where the subscript f refers to the final conditions.

Precipitation from homogeneous solution closely approaches the conditions needed for the logarithmic law. Because the precipitant is generated uniformly and gradually throughout the solution, the liquid phase maintains its homogeneity and the number of crystals formed are small compared to ordinary methods of precipitation. Large, well formed crystals are obtained in which the foreign ions are incorporated in the logarithmic type of distribution. Digestion time is relatively unimportant here because the processes which result in true equilibrium and the formation of homogeneous crystals, i.e., recrystallization and diffusion, are slow for large crystals (41).

The distribution laws are of value for comparing different methods of separation. Distribution coefficients less than unity represent less impurity in the primary substance precipitated. A coefficient equal to unity indicates identical concentrations of impurity in both precipitate and filtrate. The more the values of D and λ vary from unity, the greater the separation of the impurity from the carrier substance.

A separation in which a logarithmic type of distribution is obtained is more efficient than that which is obtained by a homogeneous distribution (assuming $\lambda = D$). Figure 2.3 illustrates curves for various values of D and λ.

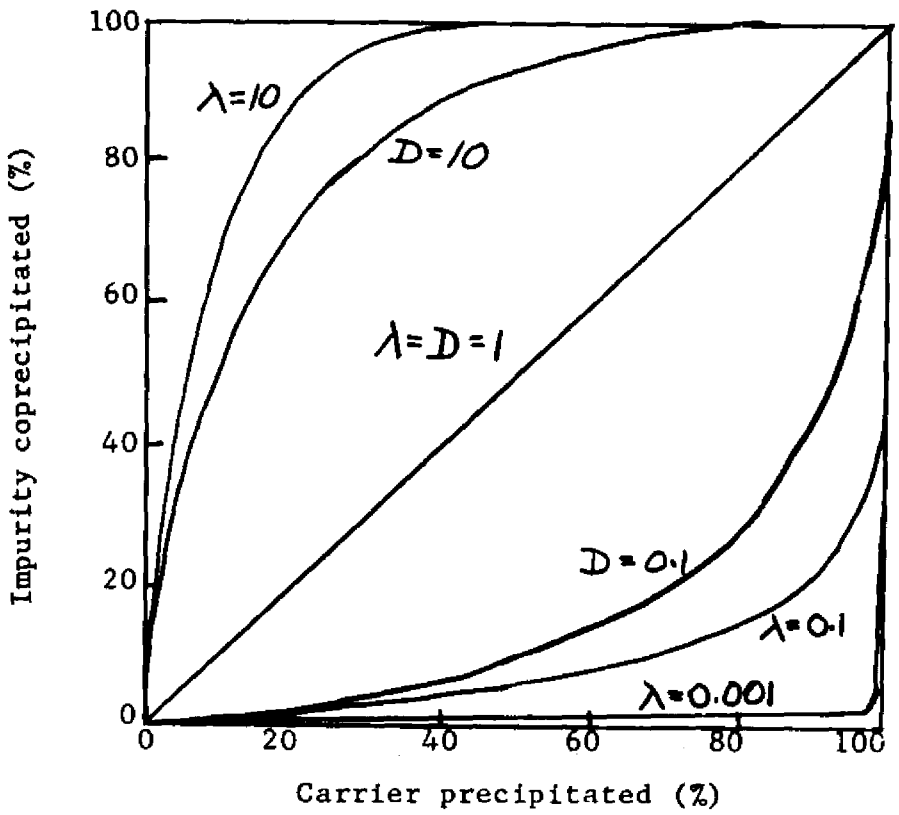


Fig. 2.3. Distribution Curves

The concept of precipitation from homogeneous solution has been known for quite some time and, in fact, was employed as a basis in several procedures in which hydrous oxides were precipitated. Among these, sodium thiosulfate and halide-halate mixtures are examples of reagents used to effect this

method of precipitation. However, the characteristics of the precipitates obtained were undesirable. In 1937 Willard and Tang published a successful method in which urea was used as a source of ammonia to slowly precipitate the basic salt of the aluminum ion (44). The success of the urea method was due primarily because of the presence of a suitable anion which encourages the formation of a dense precipitate. The precipitation of a cation as a hydroxide or basic salt requires the presence of such an anion if the precipitate is to have the desirable properties required in a gravimetric procedure. The purpose of a suitable anion may be threefold. It can serve as a buffer and thus regulate the pH change in the solution. It can become incorporated into the precipitate thus forming a basic salt. It may diminish the concentration of a cation by a complex formation. Table I lists the most suitable anions recommended for use in the precipitation of some metal ions (16).

TABLE I

SUITABLE ANIONS USED FOR UREA PRECIPITATIONS

Metal	Suitable Anion
Aluminum	Benzoate
Gallium	Sulfate
Iron	Formate
Thorium	Formate
Tin	Sulfate
Titanium	Sulfate
Zirconium	Succinate

Since Willard and Tang's work, it has been demonstrated that many anions can be generated slowly to produce precipitates with greatly improved characteristics. Some of these anions are phosphate, oxalate, iodate, sulfide, chromate and others (4, 5, 6, 13, 14, 45, 46). These anions can be generated with a variety of compounds and examples are shown below:

a) $(C_2H_5O)_3PO + 3H_2O = 3CH_3CH_2OH + H_3PO_4$

b) $(CH_3)_2C_2O_4 + 2H_2O = 2CH_3OH + H_2C_2O_4$

c) $NH_2HSO_3 + H_2O = NH_4^+ + H^+ + SO_4^=$

d) $CH_3CSNH_2 + H_2O = CH_3CONH_2 + H_2S$

e) $ClCH_2CH_2OHCH_2OH + H_2O = CH_2OHCH_2OHCH_2OH + H^+ + Cl^-$

Besides the generation of anions homogeneously, the problem of cation generation also has received a great deal of attention. This means of generating the precipitant is gaining popularity as evidenced by the many papers in the field and the last two reviews in Analytical Chemistry furnish good references (29, 30). The book by Gordon, Salutsky and Willard (16) also has fine references and examples. Examples of slowly generating the cationic precipitant are: the precipitation of silver chloride by destroying the stability of the silver-ammonia complex (15) and the release of barium and zinc from their complexes with EDTA (7, 25).

Presently, there seem to be differences of opinion with regard to the term "precipitation from homogeneous solution." A study, performed by Klein and others (22), on the nucleation and precipitation of silver chloride--formed by slow hydrolysis of allyl chloride--yielded the following results: the ion product determined from conductance measurements and the known rate of hydrolysis of the organic chloride was found to exceed the equilibrium ion product by several times during the early stages of precipitation.

But microscopic studies of the number of particles of cadmium sulfide, lead sulfide and barium sulfate in solution at several stages of precipitation from homogeneous solutions indicate the importance of nucleation sites (11). These studies by Fisher indicate that nucleation is completed within the first thirty seconds of reaction time and subsequent reaction takes place as growth on these nuclei. Fisher concludes that precipitation from homogeneous solution has little control over the number of crystal nuclei. However, Haberman and Gordon (17) disagree with this and base their opinion on the work done by Klein and others. They say that Fisher's conclusions are not valid for most cases concerning PFHS. More experimental evidence perhaps may resolve whether the term precipitation from homogeneous solution is a misnomer.

CHAPTER III

METHODS USED IN CALCIUM DETERMINATION

Methods used in the determination of calcium cover a wide spectrum ranging from the very sophisticated technique of neutron activation to the more conventional precipitation methods.

Calcium is almost always precipitated as the oxalate, $CaC_2O_4.H_2O$, after a series of initial steps aimed at the removal of interferences other than the alkali metals and the alkaline earths. The method considered best for the precipitation of calcium oxalate involves the procedure of Gordon and Chan (46) which employs the technique of PFHS. It involves the addition of oxalate ions to an acid solution containing calcium, boiling the solution with urea which neutralizes the acid throughout and leads to the formation of a coarse, crystalline precipitate

$$2H^+ + CO(NH_2)_2 + H_2O = CO_2 + 2NH_4^+ \qquad (3.1)$$

$$Ca^{++} + C_2O_4^{=} = \underline{CaC_2O_4} \qquad (3.2)$$

The precipitate is then ignited and weighed either in the form of calcium oxide or calcium carbonate. The

characteristics of these weighing forms have already been discussed.

Some of the common interferences encountered when precipitating calcium oxalate are SiO_2, CO_3^{-2}, F^-, SO_4^{-2} and large amounts of NH_4^+ (21). Barium and strontium ions are particularly bad interferences. The latter cannot be tolerated and Ba^{+2} when present in such small amounts as only 3 or 4 mg. requires double or triple precipitations to separate it from the calcium oxalate (23). Magnesium can interfere in any of several ways. This ion supposedly forms a soluble complex with oxalate and thus increases the solubility of calcium oxalate. It also contaminates the precipitate by way of coprecipitation and post-precipitation.

The oxalate method is also the basis for a titrimetric method. After the calcium oxalate is precipitated, it is filtered, washed and dissolved in acid. The liberated oxalic acid is subsequently titrated with a standard solution of potassium permanganate. This method assumes the precipitate to be 100 per cent calcium oxalate and is subject to most of the disadvantages inherent in the precipitation of calcium oxalate.

A number of cations form precipitates with naphthal-

hydroxamic acid but these can all be dissolved in ammonium hydroxide or ammonium tartrate with the exception of the alkaline earth compounds. Beck (1) has described the use of naphthalhydroxamates for the gravimetric and titrimetric determination of calcium. The precipitate is ignited and weighed as the metal naphthalhydroxamate. In the titrimetric micro-method, the calcium is precipitated by boiling with the sodium form of the acid. The precipitate is separated by centrifuging and washed with acetone. It is then suspended in 50 per cent potassium hydroxide solution and the warm solution is titrated with 0.01N potassium copper-III periodate. The endpoint is very sharp and is marked by the appearance of a green color stemming from the combination of the colors of bivalent and tervalent copper.

Ferrocyanide can also be used in a gravimetric and titrimetric determination of this Group IIA element (12). Either potassium or ammonium ferrocyanide can serve as precipitant; however, only one of the cations can be present in the gravimetric method. The calcium solution is adjusted to pH8 with sodium hydroxide and an equal volume of alcohol added. It is then heated to 50°C. and a saturated solution of the reagent in 20 per cent alcohol is added. The

resulting precipitate is filtered in a glass crucible, washed with 50% alcohol, dried at 105°C. and weighed as $K_2[CaFe(C_N)_6]$. In the titrimetric method it is dissolved in 5 per cent sulfuric acid and titrated, preferably with ceric sufate using ferroin as the indicator.

Ethylenediaminetetraacetic acid (EDTA), of course, is well known for the titrimetric analysis of calcium. There are various indicators which can be used with this method and Calcon is among the best available (20). As is to be expected, masking agents must be used to avoid the interferences of those cations which form complexes with EDTA. Phosphate al presents a problem when the calcium and phosphate ion product exceeds the solubility product of calcium diphosphate. Phosphate is best removed by ion-exchange (9).

Pyrogallolcarboxylic acid provides a colorimetric determination of 0.2-0.4 mg. calcium in 10ml of solution (36). The procedure here is to add 1ml 2N sodium hydroxide and 2ml of 2 per cent starch, dilute to 50ml with saturated reagent solution and measure the blue-violet color at 570 mμ. The main interferences here are: Sr^{+2}, Ba^{+2}, Sn^{+2}, PO_4^{-3}, F^-, $C_2O_4^{-2}$, and CO_3^{-2}.

Newer methods of instrumental analysis are also used in calcium determinations. The use of flame photometry for its determination may give high values for the metal when sodium and potassium are present. A common procedure for circumventing their interference is to separate the calcium as the oxalate, dissolve the precipitate with acid and make the subsequent flame photometric measurement (42). Other ions such as Al^{+3}, SO_4^{-2} and PO_4^{-3} may interfere. The bands at 554 mμ and 622 mμ or the line at 422.7 mμ can be used for making measurements.

Atomic absorption spectrophotometry is another instrumental technique used in the determination of the alkaline earth metal. There are various interferences, however, which detract from this attractive analytical method. Such ions as CO_3^{-2}, Br^-, SO_4^{-2}, NO_3^-, VO_3^-, F^-, Al^{+3}, Be^{+2}, Ti^{+4} and others suppress the calcium absorption to some degree. Detergents also act as interfering agents. West, Ramakrishna and Robinson have studied the elimination of such interferences in work soon to be published (43). The band normally used for the absorption readings is that at 212 mμ.

The above brief discussion on methods for calcium

analysis is not intended to imply a thorough review of the subject. Its purpose is merely to point out the various and diverse techniques which can be used, those described being the more common ones employed. There are other methods involving fluorescence, polarography, chromatography, neutron activation, etc., which are also employed but their use is less common and more limited.

CHAPTER IV

ATOMIC ABSORPTION SPECTROPHOTOMETRY

A. INTRODUCTION

Over the past twenty-five years there have been rapid advances in inorganic analytical chemistry. Some of these advances have included the development of improved colorimetric procedures and excellent spectrophotometers for determining optical densities of colored solutions at narrowly defined wavelengths. Such tools as polarography, emission spectrometry, X-ray fluorescence, flame photometry, etc., are commonly in use by the analytical chemist.

These various physical methods of analysis have developed to their present stage by a fundamental investigation and appreciation of atomic or molecular characteristics, and the useful interpretation attained by combining the efforts of both the physicist and chemist.

Atomic absorption spectrophotometry is one of these fields which has become of paramount importance and a common tool for the analytical chemist. It is not a panacea for the problems often encountered in analysis such as specificity,

sensitivity, interferences, speed, blanks, etc. It does, however, provide many favorable solutions to these problems as shall be subsequently seen. Atomic absorption spectrophotometry is of great value for trace metal analysis in such fields as chemicals manufacture, agriculture, medicine, air and water pollution which are concerned with traces of metals in the vicinity of a few parts per million.

The phenomenon of atomic absorption is not a new one and it has been employed by scientists for some time. This is the phenomenom which is responsible for the Fraunhofer lines. Scientists use it to detect elements in the relatively cool gases enveloping stars and to measure flame temperatures. In 1955 Walsh (39) demonstrated that the technique of atomic absorption could serve as a basis for analysis.

B. THEORY

Ground state atoms make up the bulk of an atomic population under most conditions when dealing with emission methods. The sample is atomized and excited, the emitted radiation dispersed, and the intensities of the selected lines in the emission spectrum measured. In the case of atomic absorption, however, the fraction of energy of a

specific wavelength that is absorbed serves as a measure of the concentration of the absorbing species.

The amount of light absorption is a function of the number of atoms in the light path and the ability of each atom to absorb. If the atomization conditions are constant, the fraction of atoms in the light path is proportional to the concentration of metal in the sample. This fact, then, serves as the basis for the application of atomic absorption to analytical chemistry. The tendency of each atom to absorb is a physical property of the individual atom involved. The laws governing atomic absorption are well known,

$$I = I_o e^{-K_\nu l} \qquad (4.1)$$

where

I = intensity of the light after having passed through the absorption medium.

I_o = initial intensity of the collimated beam of monochromatic light.

K_ν = absorption coefficient of the vapor at frequency ν

l = thickness of the atomic vapor.

The atomic absorption lines are usually extremely narrow, and subject to variation in shape due to changes in physical conditions such as temperature and pressure. The integrated

absorption coefficient is independent of the shape of the line. Its measurement, however, yields a reliable means of analysis. By classical dispersion theory, the relationship between integrated absorption and concentration is given by,

$$\int K_\nu d_\nu = \frac{\pi e^2}{mc} N_\nu f \qquad (4.2)$$

where,

e = electronic charge

m = electronic mass

c = light velocity

N = number of atoms per cm^3 which can absorb in the range ν to $\nu + d\nu$

f = oscillator strength of the transition

Thus, for a transition initiated from the ground state, where N differs very little from N_o (number of atoms in the ground state), the integrated absorption is proportional to the concentration of free atoms in the absorbing medium and is independent of the temperature of the vapor. In the case of flame emission photometry, the emission intensity is directly proportional to the number of excited atoms which in turn depends on the temperature. The temperature independent reading is one of the main attractions of the atomic absorption

method.

Unfortunately, it is not feasible to apply equation (4.2) directly. There is no satisfactory means of determining the integrated absorption coefficient by conventional scanning methods, since the width of the spectral lines under the usual conditions of measurement is in the range of 0.02-0.1A. Most monochromators cannot effect the resolution required to record the profiles of such lines. The method which has been adopted to measure the profile of an absorption line, is that which measures the coefficient of absorption at the center of the line. This is done by using an atomic line source which emits lines having a much smaller half-width than the absorption lines so that, to a good approximation, a measurement can be made of peak absorption. The latter is proportional to the concentration if the width and shape of the lines does not depend on the concentration.

C. APPARATUS

The essential components of an atomic-absorption spectrophotometer include:

(a) sharp line source

(b) atomizer

(c) wavelength selector

(d) intensity measurement and recording equipment

A schematic diagram showing the basic components of an atomic absorption spectrophotometer is shown in Fig. 4.1. The chopper serves to modulate the light beam from the source.

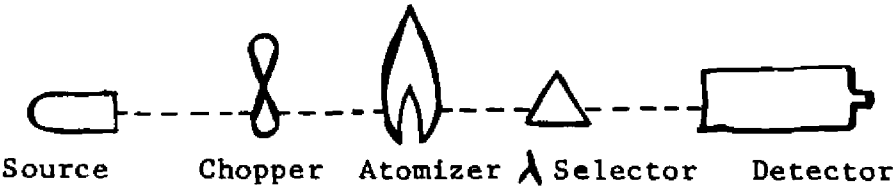


Fig. 4.1. Schematic diagram of the basic components in an atomic absorption spectrophotometer.

a) Sharp Line Source

Ideally the light source should emit resonance radiation of the element under examination with a line half-width much less than the Doppler width of the absorbing line. Hollow cathode lamps are the most useful and most often used sources for sharp resonance lines. These lamps may be obtained commercially for more than thirty different elements. Hollow cathode lamps are simply hollow cylinders made from material containing the element in question, enclosed in a glass

envelope having a glass or quartz window. A low pressure inert-gas atmosphere is maintained in the envelope. The lamp is energized by a potential of about 400V with currents up to 100mA. The spectrum of the glow discharge is representative of the cathode material and the carrier gas.

b) Atomizer

Conventional atomizers and burners have been the main devices used for vaporization of the sample. As in the case of flame photometry, the atomizer should insure a reproducible supply of fine droplets of solution. The best atomizer will produce the largest number of droplets vaporized into the flame per unit time.

Burners that have been used are the Beckman flame photometer burner, the Hilger and Watts atomic absorption attachment burner and the forced feed burner. More detailed information on atomizers as well as on the topic of atomic absorption spectroscopy is found in the works of Elwell and Gidley (10) and Robinson (34).

c) Wavelength Selector

Filters from Bausch and Lomb are used in the determination of sodium, potassium and calcium. However, filters do not always yield the necessary resolution of spectral lines

and in such instances, a good monochromator is necessary for selecting the required wavelength. The most versatile wavelength selection system is a monochromator capable of variable wavelength selection. Quartz prism spectrographs and modified ultraviolet spectrophotometers have been used for this purpose.

d) Intensity Measurement and Recording Equipment

In atomic absorption spectrophotometry no special methods are necessary for measuring light intensity, and the standard methods serve quite well. If the instruments use either interference or colored filters for wavelength selection, a simple barrier-layer photocell and galvanometer can be used for intensity measurement. In most other cases, however, photomultiplier detectors are the most useful. These detectors cover a wide wavelength range and are very sensitive, their sensitivity being controlled by the voltage applied at the dynodes. The high sensitivity of the photomultiplier tubes allows narrow slit widths and low lamp currents to be used.

CHAPTER V

EXPERIMENTAL RESULTS

A. APPARATUS

The atomic absorption spectrophotometer used for the investigation of the filtrate was the Perkin-Elmer 303. A hollow cathode calcium lamp built by Ransley Glass Instruments was used as the light source. It was operated with a current of 20mA. The atomizer was a large bore Beckman burner #4060. The slit and wavelength settings were 5 mμ and 212 mμ respectively. The oxygen flow rate was 4.5 l./min. and that for hydrogen 18 l./min. The aspiration rate for the sample ws 4 ml./min.

The calcium fluoride precipitate was contained in a platinum crucible and ignited to 800°C. in a Hevi-Duty muffle furnace. All weighings were performed with a Mettler H-6 balance and a Beckman model G pH meter was used for pH measurements.

B. SOLUTIONS

Double distilled water was used in the preparation of all solutions. Chemicals used were of reagent grade unless

otherwise specified. All solutions were stored in polyethylene bottles.

1. Ethylenediaminetetraacetic acid (EDTA)

A 0.100M EDTA solution was prepared by weighing 29.210g of the acid (dried at 130°C. for 2 hours) and placing it in 600 ml. of water. The acid was then dissolved with 50% sodium hydroxide and the final solution diluted to one liter. The sodium hydroxide used was 50% by weight as used for Kjeldahl determination, and packed in polypropylene containers.

2. Calcium

A solution containing 0.100g Ca/10 ml was prepared by dissolving 24.973g of calcium carbonate (dried at 120°C. for 4 hours) in hydrochloric acid. After diluting the solution to one liter, the strength was checked by standardizing with EDTA using murexide as the indicator.

3. Magnesium

A solution containing 0.100g. Mg/10 ml was prepared by dissolving, in hydrochloric acid, 16.579g magnesium oxide (dried at 120°C. for 4 hours). After diluting the solution to one liter, aliquots were taken and the strength checked by titrating with 0.0100M EDTA using Eriochrome Black T

as the indicator.

4. Lead

A solution containing 0.100g. Pb/10 ml. was prepared by dissolving 7.9930g lead nitrate, (dried at 120°C. for 4 hours), in water containing 5 ml. of nitric acid. The solution was diluted to a final volume of one liter.

5. Barium

A solution containing 0.100g. Ba/10 ml. was prepared by dissolving 3.7928g $BaCl_2.2H_2O$, (dried at 120°C. for 4 hours), in water. The solution was diluted to a final volume of 250 ml.

6. Sodium

A solution containing 0.100g. Na/10 ml. was prepared by dissolving 6.3548g NaCl, (dried at 120°C. for 3 hours), in water. The solution was diluted to a final volume of 250 ml.

7. Miscellaneous Reagents

The urea, and ammonium chloride used were Fisher certified reagents. Baker & Adamson fluoboric acid (48%-50%) was used as the source of fluoride ions. Perchloric acid (60%B & A) was used to eliminate the fluoride ion interference in the atomic absorption readings for calcium.

8. Wash Solution

The wash solution was prepared by dissolving 30g ammonium fluoride in one liter of double distilled water.

C. PRELIMINARY STUDIES ON THE PRECIPITATION OF CALCIUM AS THE FLUORIDE FROM HOMOGENEOUS SOLUTION

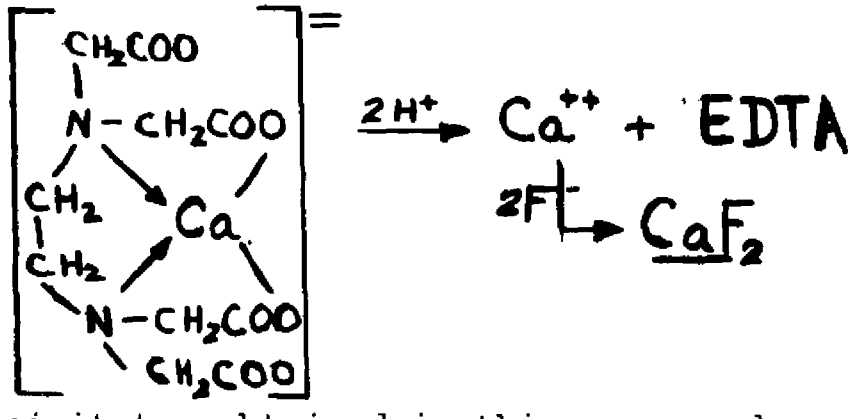
Shaver and Gordon (18) state that calcium fluoride can be slowly precipitated by hydrolyzing ethylenechlorohydrin in a solution containing the calcium complex of ethylenediaminetetraacetic acid and potassium fluoride. They do not describe any of the characteristics of the precipitate nor do they say whether the precipitation is suitable for analytical purposes.

Initially, a similar approach was attempted in this investigation. To solutions containing the calcium complexes of ethylenediaminetetraacetic acid, diethylenediaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA); ammonium fluoride (or sodium fluoride) and β-hydroxyethylacetate were added. Before the addition of these reagents the starting solutions were at pH 9-10, however, upon their addition the solutions turned turbid either immediately or 2-3 minutes later due to the hydrolysis of the acetate. Concentrated ammonium hydroxide was then used to return the solution to

pH 9-10 and thus remove the turbidity. The samples were then placed on a hot plate. After 10-15 minutes a slight turbidity formed indicating the precipitation of calcium fluoride. Upon hydrolysis, B-hydroxyethylacetate yields acetic acid,

$$CH_3COOCH_2CH_2OH + H_2O = CH_3COOH + CH_2OHCH_2OH \quad (5.1)$$

and thus decreased the pH of the solution which in turn reduces the stability of the calcium complex. The concentration of calcium ions reaches a certain critical value and with the fluoride ions in solution, the precipitation of calcium fluoride is initiated, e.g.,



The precipitates obtained in this manner, however, were extremely gelatinous. Furthermore, a sufficient amount of the hydrolyzing agent could not be added at one time because of its ease of hydrolysis. Consequently, periodic additions of the reagent were necessary during the reaction in order to bring the solution to pH6. (The recommended pH range

found in the literature is 4.5-5.4). Figure 5.1 is a photomicrograph of a precipitate obtained by this method.

The homogeneous generation of calcium ions from a complex in acidic solution was then investigated. For this purpose, sodium hexametaphosphate was employed as the complexing agent. Urea was used as the hydrolyzing agent, ammonium fluoride as the precipitant and the solution was regulated to pH2 and placed on the hot plate (73^{o}C.). After about 20 minutes of heating, precipitation took place. The precipitates obtained in this manner were colloidal and gelatinous and neither buffering agents such as ammonium chloride nor temperature regulation of the rate of hydrolysis of urea helped to improve the characteristics of the calcium fluoride produced.

Other attempts were made to precipitate the calcium starting from acidic solutions. For example, the simultaneous generation of <u>both</u> calcium and fluoride ions (using hexametaphosphate and the fluoborate anion) also proved fruitless. Although the precipitates were no longer gelatinous, they were colloidal in nature and tended to adhere to the beaker walls. Moreover, the precipitate now exhibited strong tendencies to creep. The "decreasing solubility" method was also

Fig. 51. Photomicrograph of calcium fluoride produced from homogeneous solution (300X).

tried. Calcium fluoride is the salt of a strong base and a weak acid which makes it somewhat soluble in very acidic solutions. Taking this fact into consideration, solutions were prepared containing calcium, ammonium fluoride, and urea at pH2. The solutions were then placed on the hot plate. As the urea hydrolyzed, the pH of the solution increased which caused a corresponding decrease in the solubility of the calcium fluoride. This method with various modifications also yielded unsatisfactory results.

Although the fluoborate ion is very stable, it was hoped that there might be a way of establishing a suitable rate of its hydrolysis to yield a precipitate of calcium fluoride with desirable analytical properties. Solutions containing fluoboric acid and calcium chloride were heated at different temperatures and in the presence of various hydrolyzing agents which decreased the acidity of the solutions. Urea, acetamide and formamide were used for this purpose. Urea was found to give the least colloidal precipitates and was chosen for subsequent investigation. The colloidal solutions probably resulted from the fast rate of hydrolysis. A sudden rise in the alkalinity of the solution favors the sudden drastic increase in the fluoride ion

concentration which leads to the formation of an abnormally large number of nucleation centers. The rates of hydrolysis of acetamide and formamide are greater than that for urea at the same temperature and perhaps this is why the solutions resulting from the former are more colloidal.

D. STUDIES ON THE CONDITIONS AFFECTING THE PRECIPITATION OF CALCIUM FLUORIDE

Because the use of fluoboric acid and urea yielded a precipitate that was not gelatinous and one which did not adhere to the beaker walls, investigations were performed to minimize some of the less desirable characteristics of the calcium fluoride such as creeping and small particle size. Tests on the filtrate with glyoxal-bis-2-hydroxyanil gave negative or faintly positive results. This indicated that the reaction could be made quantitative.

By holding the other parameters constant in the recommended procedure, each of the following were varied individually.

1. Effect of pH. The acidity of the solution, as shown in Table II, controls the amount of calcium fluoride precipitated. The final pH of the solution was regulated by varying the quantity of urea and ammonium chloride added. Quantities

TABLE II

Effect of pH on the Precipitation of Calcium Fluoride[1]

(Calcium taken: 0.1998g)

No.	pH at which turbidity appears	Final pH[2]	Difference in g
1	1.7	3.0-3.5	-0.0080
2	1.7	3.0-3.5	-0.0074
3	1.8	3.0-3.5	-0.0090
4	1.7	3.5-4.1	-0.0072
5	1.8	3.5-4.1	-0.0061
6	1.7	3.5-4.1	-0.0055
7	1.8	4.1-4.6	-0.0030
8	1.9	4.1-4.6	-0.0032
9	1.8	4.1-4.6	-0.0015
10	1.9	4.6-5.0	-0.0011
11	1.8	4.6-5.0	-0.0008
12	1.9	4.6-5.0	-0.0007
13	1.8	5.0-6.1	-0.0007
14	1.9	5.0-6.1	-0.0006
15	1.8	5.0-6.1	+0.0003

[1]Recommended procedure with modified amounts of buffer constituents to obtain varying final pH values.

[2]Initial pH of 1.6 for all determinations.

ranging from 2.0 to 8.0g were used. Upon the slightest sign of turbidity, aliquots of the solution were taken and immediately cooled to room temperature in ice water baths. The pH of each aliquot was then measured.

2. Effect of Reaction Temperature. It was found that heating the solutions with the hot plate set at low (60°C.) and the beaker partially covered, required waiting periods of more than one hour before any signs of precipitation were seen. With the hot plate set on medium (88°C.) the time of induction was 30-35 minutes. At the highest setting of the hot plate (97°C.), the induction time was reduced to 15-20 minutes.

An induction time of one hour or more is not desirable and only the two higher temperatures were investigated further.

At all three temperatures the size of the particles produced differed little as seen under the microscope. It was found, however, that the precipitate required a longer length of time for it to completely settle to the bottom of the beaker when it was formed at 88°C. than at 97°C. At 88°C., the lapse of time between the initial placing of the solutions on the hot plate to the point where the

precipitate and the supernatant liquid were clearly defined was about three hours. At 97°C., the time interval was two hours. This result plus the fact that the other reaction temperatures did not yield any better precipitates indicated the higher temperature to be the more desirable one for the precipitation.

3. Effect of the Ammonium Ion. In the absence of ammonium ions, the precipitated calcium fluoride was slightly colloidal and exhibited a tendency to creep. Also, the precipitate when seen under the microscope was less crystalline than that produced in the presence of ammonium ion.

Amounts in the range of 2.0 to 8.0g of ammonium chloride or ammonium nitrate were investigated for their effect on the precipitation process. The results obtained indicated that it did not matter what anion was associated with the ammonium ion. Since the calcium was in the form of the chloride, ammonium chloride was selected for the recommended procedure.

Of the various quantities of buffering agent used, it was found that amounts of five grams or more were instrumental in the production of a more crystalline precipitate with lesser creeping tendencies. The precipitate was not colloidal.

4. Aging and Filterability of Precipitate. Table III illustrates the effect of time interval involved between the precipitation of the calcium fluoride and its filtration.

5. Filter Paper. The filter papers used were Whatman #40 and #44 as well as Munktells 0.00H. Usually, any of the three papers gave satisfactory results but occasionally a low result was obtained with Whatman #40 as shown in Table IV.

6. Wash Solutions. Solutions of either ammonium nitrate or ammonium fluoride were used and found to be satisfactory. A solution containing 3g ammonium fluoride in 100 ml of double distilled water was adopted for the recommended procedure.

Acidic solutions were also tried since they have been recommended in the literature (27). For example, a wash solution containing 1% acetic acid and 5% ammonium nitrate was investigated but it was found that it tended to dissolve the calcium fluoride precipitate.

7. Effect of Excess Precipitant. The results obtained by using various amounts of fluoboric acid in excess of the recommended procedure is shown in Table V and Figure 5.2.

TABLE III

The Aging of the Precipitate and its Effect on Quantitative Results[3]

(Calcium added 0.1998g)

Time of standing[4]	Calcium obtained(g)	Ca in filtrate[5](g)
15 min.	0.1980	0.0009
	0.1975	0.0013
	0.1965	0.0019
1 hr.	0.1985	0.0003
	0.1980	0.0008
	0.1986	0.0006
3 hrs.	0.1992	0.0000
	0.1996	0.0000
	0.1992	0.0001
8 hrs.	0.1992	0.0000
	0.1997	0.0000
	0.1994	0.0000
24-32 hrs.	0.1992	0.0000
	0.2001	0.0000
	0.1997	0.0002

[3]Aged at 20°C.

[4]Time of hydrolysis is 2 hours

[5]By atomic absorption

TABLE IV

Results Obtained with Different Filter Papers[6]

(Calcium taken: 0.1998g)

Filter Paper	Calcium obtained[7] (g)
Whatman #40	0.1992
	0.1992
	0.1994
	0.1985
Whatman #44	0.1994
	0.1992
	0.2004
	0.1995
Munktells 0.00H	0.1992
	0.1995
	0.2000
	0.1994

[6]Using the recommended waiting period

[7]Representative values

TABLE V

The Effect of Excess Precipitating Agent

on the Weight of Precipitate Produced

Recommended Vol. of HBF_4 (ml)	Vol. of HBF_4 used (ml)	Wt. of CaF_2 expected (g)	Wt. of Precipitate (g)
0.7-1.0	1.5	0.1946	0.1965
0.7-1.0	1.5	0.1946	0.1959
0.7-1.0	1.5	0.1946	0.1950
1.0	2.0	0.3892	0.3932
1.0	2.0	0.3892	0.3943
1.0	2.0	0.3892	0.4889
1.5	3.0	0.4866	0.4915
1.5	3.0	0.4866	0.4927
1.5	3.0	0.4866	

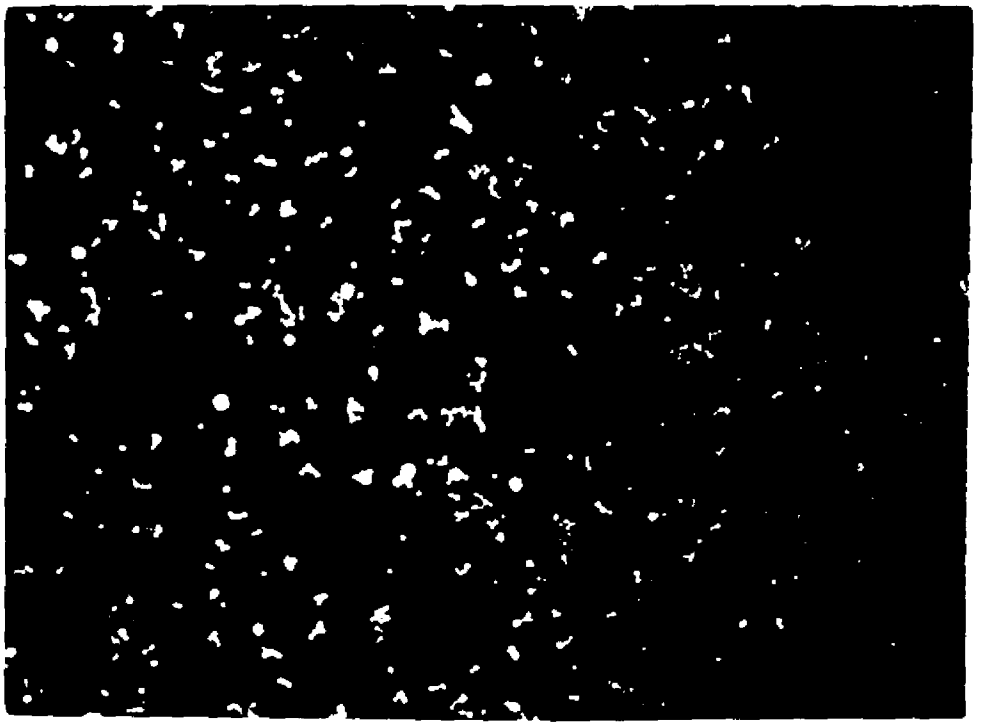


Fig. 5.2. The effect of excess precipitating agent on the character of calcium fluoride.

E. INVESTIGATION OF THE FILTRATE

The filtrate was investigated by means of atomic absorption spectrophotometry. The fluoride ion suppresses the calcium readings and is thus an interference in its determination. Various masking agents and acids were considered for the elimination of this interference; among them were Fe^{+3}, Al^{+3}, Zr^{+4}, HCl, HNO_3, $HClO_4$, H_3BO_3+HCl, EDTA and DTPA. Of these, 60% $HClO_4$, (Baker & Adamson) was found to remove the fluoride interference. Higher concentration of this acid as well as Merck's 60% $HClO_4$ were not suitable because they imparted a substantial enhancement in the atomic absorption readings. Table VI shows the optical density readings for calcium solutions in the 5-50 parts per million range. Columns A and B are the readings obtained for these same calcium concentrations in the presence of 50 and 100 parts per million of fluoride ions. Column C refers to the readings obtained with 100 parts per million fluoride and 2 ml. $HClO_4$. Figure 5.3 illustrates these results in graphic form.

F. INTERFERENCES

Magnesium, lead, barium and sodium were investigated as

TABLE VI

The Effect of Fluoride Ions on the Optical Density Readings for Calcium at Various Concentrations

Ca (ppm)	O.D.	A	B	C
5	0.038	0.005	0.001	0.039
10	0.079	0.010	0.002	0.086
15	0.122	0.021	0.005	0.124
20	0.156	0.043	0.021	0.159
25	0.188	0.054	0.044	0.187
35	0.216	0.092	0.057	0.212
50	0.359	-	-	-

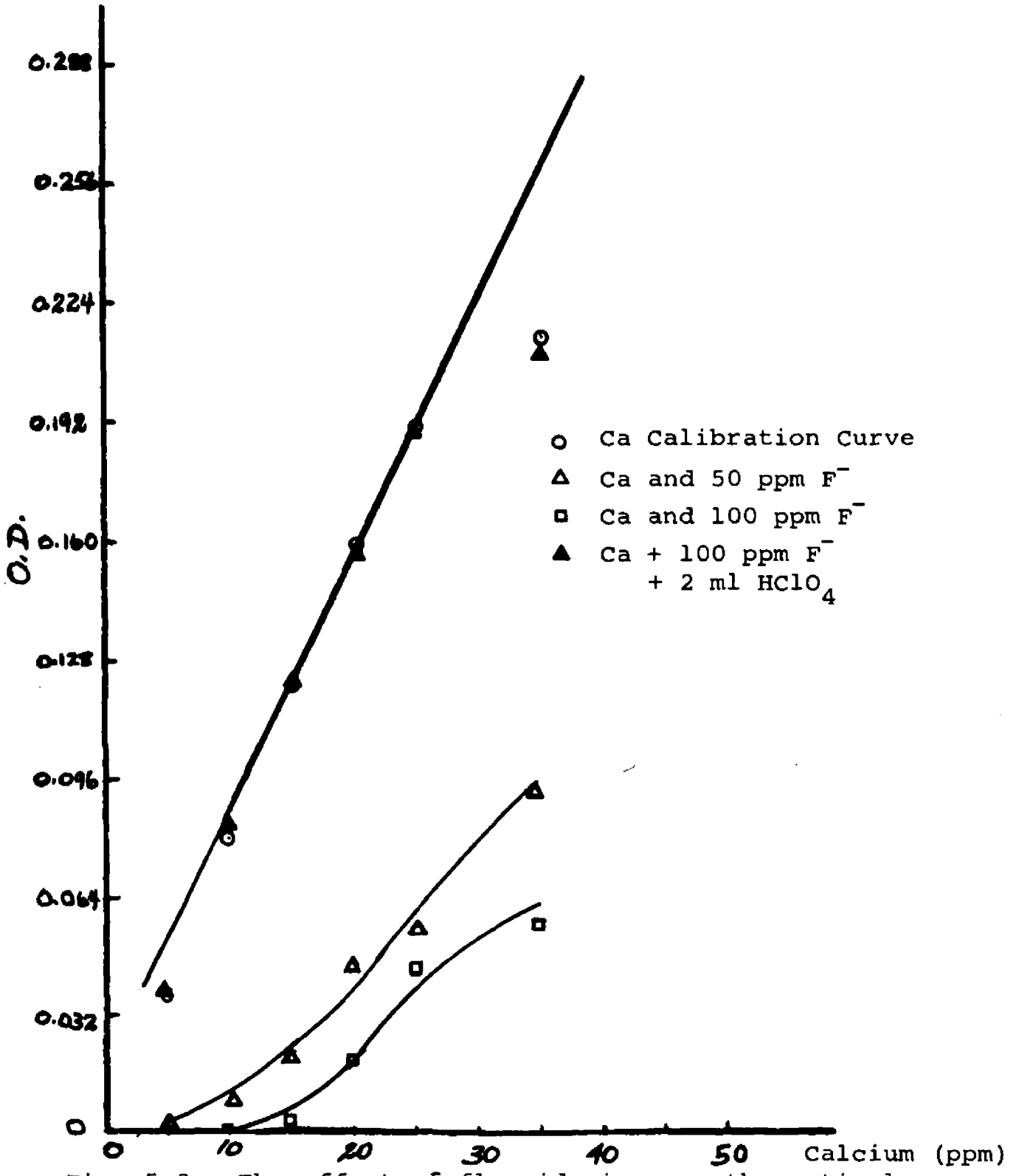


Fig. 5.3. The effect of fluoride ions on the optical density readings for calcium.

substances which would probably interfere with the determination of calcium. Of these, it was found that magnesium and lead interfered in all concentrations studied but that barium and sodium could be tolerated in certain amounts. Tables VII-X illustrate this.

G. RECOMMENDED PROCEDURE

Add 1.0 ml of fluoboric acid and 5.0g. ammonium chloride to 100 ml of a solution containing 0.1-0.2g. calcium. Dilute to 200 ml and add 6.5g. of urea. Partially cover the beaker containing the solution and heat on a hot plate set at about 95^{o}C. Allow the precipitate which forms to stand for at least three hours before filtering with Whatman #44 filter paper. Wash the precipitate 5 times with 10 ml of portions of 3% ammonium fluoride and twice with 10 ml portions of distilled water. Transfer the filter paper to a previously weighed platinum crucible and carbonize it with the aid of a Tirrill burner. Place the crucible for approximately 20 minutes in a muffle furnace at 800^{o}C. then cool and weigh. The theoretical gravimetric factor for converting calcium fluoride to calcium is 0.5133.

Tables XI-XIII illustrate the results obtained with this

TABLE VII

Determination of Calcium as the

Fluoride in the Presence of Magnesium

Mg added (g)	Final pH	CaF_2 taken (g)	CaF_2 found (g)	Diff. (g)
0	5.7	0.3892	0.3898	+0.0006
0.05	5.5	0.3892	0.5045	+0.1153
0.05	5.3	0.3892	0.5034	+0.1142
0.05	5.5	0.3892	0.5051	+0.1159
0.05	5.2	0.3892	0.5044	+0.1152
0.02	5.6	0.3892	0.4270	+0.0378
0.02	5.5	0.3892	0.4248	+0.0356
0.02	5.7	0.3892	0.4275	+0.0383

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TABLE IX

Determination of Calcium as the Fluoride

in the Presence of Barium

Ba added (g)	Final pH	CaF_2 taken (g)	CaF_2 found (g)	Diff. (g)
0	5.7	0.3890	0.3881	-0.0009
0.05	5.6	0.3890	0.3948	+0.0051
0.05	5.6	0.3890	0.3936	+0.0046
0.04	5.7	0.3890	0.3899	+0.0009
0.04	5.6	0.3890	0.3916	+0.0026
0.04	5.6	0.3890	0.3902	+0.0012
0.04	5.7	0.3890	0.3902	+0.0012
0.02	5.7	0.3890	0.3895	+0.0005

TABLE X

Determination of Calcium as the Fluoride

in the Presence of Sodium

Na added (g)	Final pH	CaF_2 taken (g)	CaF_2 found (g)	Diff. (g)
0	5.6	0.3901	0.3886	-0.0015
0.1	5.8	0.3901	0.3928	+0.0027
0.1	5.7	0.3901	0.3920	+0.0019
0.1	5.8	0.3901	0.3923	+0.0022
0.05	5.7	0.3901	0.3912	+0.0011
0.05	5.8	0.3901	0.3909	+0.0008
0.05	5.7	0.3901	0.3907	+0.0006

TABLE XI

Determination of Calcium Alone by

Precipitation as Calcium Fluoride

Calcium taken (g)	Calcium found (g)	Calcium in filtrate	Diff. (g)
0.0999	0.0994	0.0001	-0.0005
0.0999	0.0996	0.0000	-0.0003
0.0999	0.1000	0.0001	+0.0001
0.0999	0.0996	0.0002	-0.0003
0.0999	0.0999	0.0000	0.0000
0.0999	0.0996	0.0000	-0.0003
0.0999	0.0996	0.0001	-0.0003
0.0999	0.0994	0.0000	-0.0005
0.0999	0.0998	0.0001	-0.0001
0.0999	0.0998	0.0000	-0.0001
0.0999	0.0997	0.0005	-0.0002

TABLE XII

Determination of Calcium Alone by

Precipitation as Calcium Fluoride

Calcium taken (g)	Calcium found (g)	Calcium in filtrate (g)	Diff. (g)
0.1998	0.1992	0.0003	-0.0006
0.1998	0.1992	0.0001	-0.0006
0.1998	0.2001	0.0000	+0.0003
0.1998	0.2004	0.0001	+0.0006
0.1998	0.1992	0.0002	-0.0006
0.1998	0.1997	0.0000	-0.0001
0.1998	0.2004	0.0000	+0.0006
0.1998	0.1998	0.0000	0.0000
0.1998	0.1996	0.0000	-0.0002
0.1998	0.2000	0.0000	+0.0002
0.1998	0.1996	0.0002	-0.0002
0.1998	0.1994	0.0003	-0.0004

TABLE XIII

Determination of Calcium Alone by Precipitation as Calcium Fluoride[9]

Calcium taken (g)	Calcium found (g)	Calcium in filtrate	Diff. (g)
0.2498	0.2507	0.0002	+0.0007
0.2498	0.2498	0.0000	0.0000
0.2498	0.2505	0.0001	+0.0007
0.2498	0.2493	0.0001	-0.0005
0.2498	0.2507	0.0000	+0.0009
0.2498	0.2498	0.0000	0.0000
0.2498	0.2507	0.0000	+0.0009
0.2498	0.2500	0.0002	+0.0002

[9] 1.5 ml. of fluoboric acid added.

procedure. Table XIV expresses the amounts of calcium obtained in terms of calcium fluoride and calcium sulfate. The sulfate precipitate was obtained by adding dilute sulfuric acid to the calcium fluoride, evaporating the excess acid and heating the resulting precipitate for 20 minutes at 800°C. Table XV shows that the calcium fluoride obtained is not hygroscopic.

Figures 5.5 - 5.7 are representative of the calcium fluoride crystals obtained with the recommended procedure. Figure 5.8 is a photograph of calcium fluoride produced by Baker and Adamson introduced here merely to show the contrast. The scale in Figure 5.4 allows for approximating the size of the crystals.

TABLE XIV

Quantities of Calcium Expressed As

Calcium Fluoride and Calcium Sulfate

CaF_2 expected (g)[10]		CaF_2 obtained (g)	Diff. (g)	$CaSO_4$ expected	$CaSO_4$ obtained	Diff. (g)
0.1946		0.1946	0.0000	0.3384	0.3381	-0.0003
0.1946		0.1945	-0.0001	0.3384	0.3394	+0.0010
0.1946	I	0.1948	+0.0002	0.3384	0.3381	-0.0003
0.1946		0.1943	-0.0003	0.3384	0.3380	-0.0004
0.3382		0.3898	+0.0006	0.6788	0.6781	-0.0007
0.3892		0.3904	+0.0012	0.6788	0.6778	-0.0010
0.3892	II	0.3907	+0.0015	0.6788	0.6780	-0.0008
0.3892		0.3899	+0.0009	0.6788	0.6777	-0.0011
0.4866		0.4880	+0.0014	0.8466	0.8470	+0.0004
0.4866	III	0.4856	-0.0010	0.8466	0.8476	+0.0010

[10] I, II, and III refer to the calcium fluoride expected respectively from 0.0999g, 0.1998g and 0.2498g calcium added.

TABLE XV

Results Showing that the Calcium

Fluoride Obtained is not Hygroscopic

Time	Weight
0	0.3898[11]
1 hr.	0.3898
4 hrs.	0.3898
8 hrs.	0.3899
1 day	0.3898
2 days	0.3898
5 days	0.3898
7 days	0.3899

[11] Initial weight

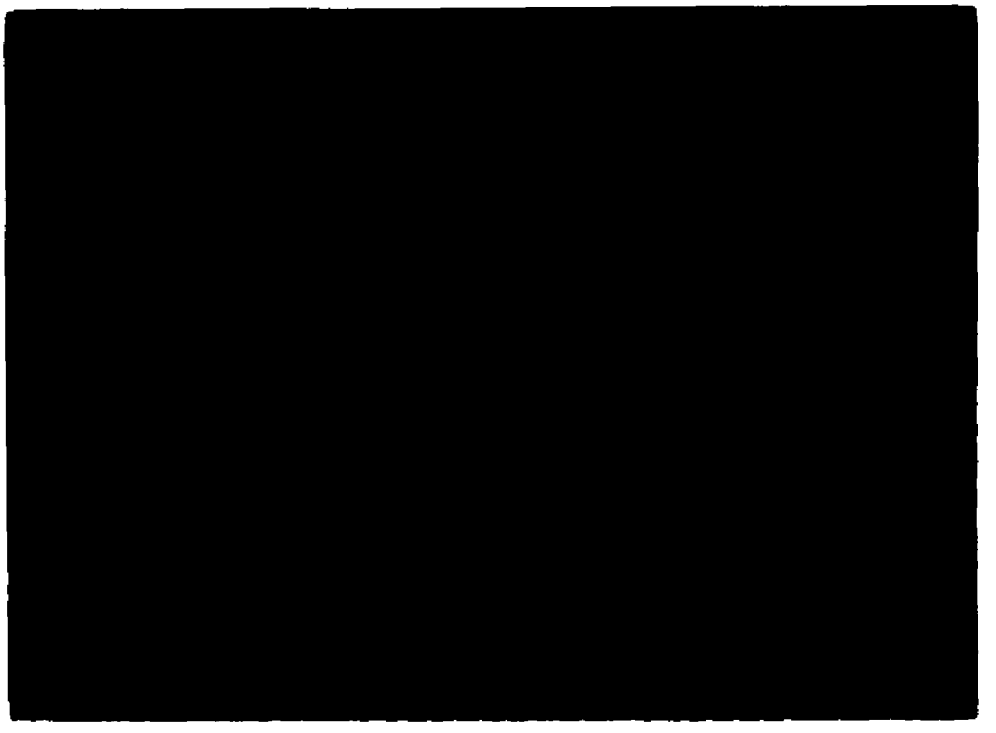

Fig. 5.4. Scale for approximating the size of the calcium fluoride crystals (300x). Each small division represents 10μ and each large division 100μ.

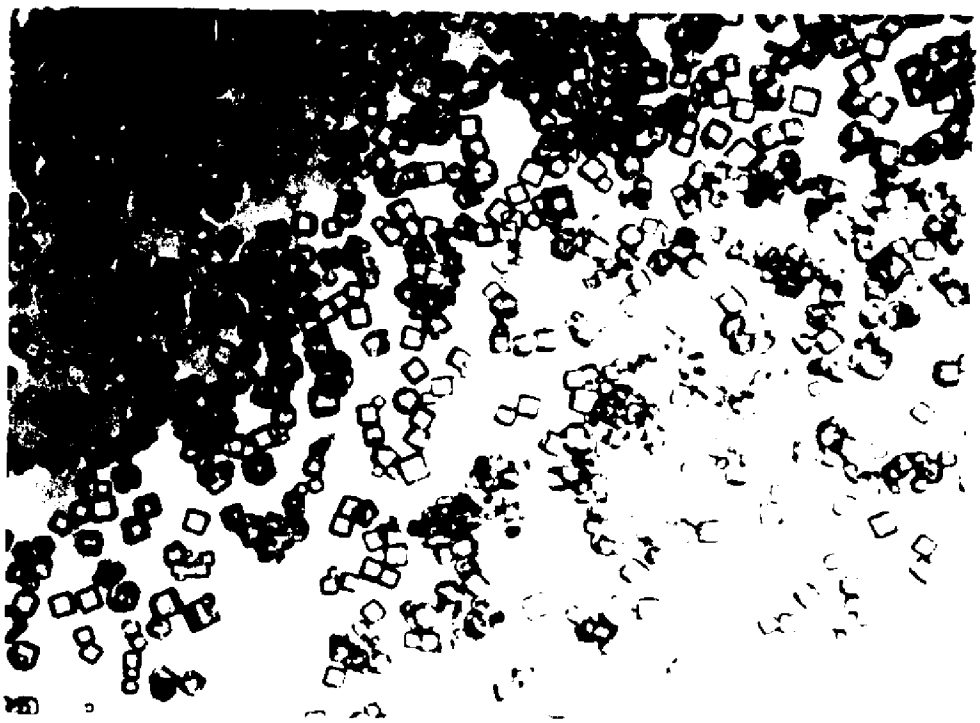

Fig. 5.5. Photomicrograph of calcium fluoride produced from homogeneous solution (300x).

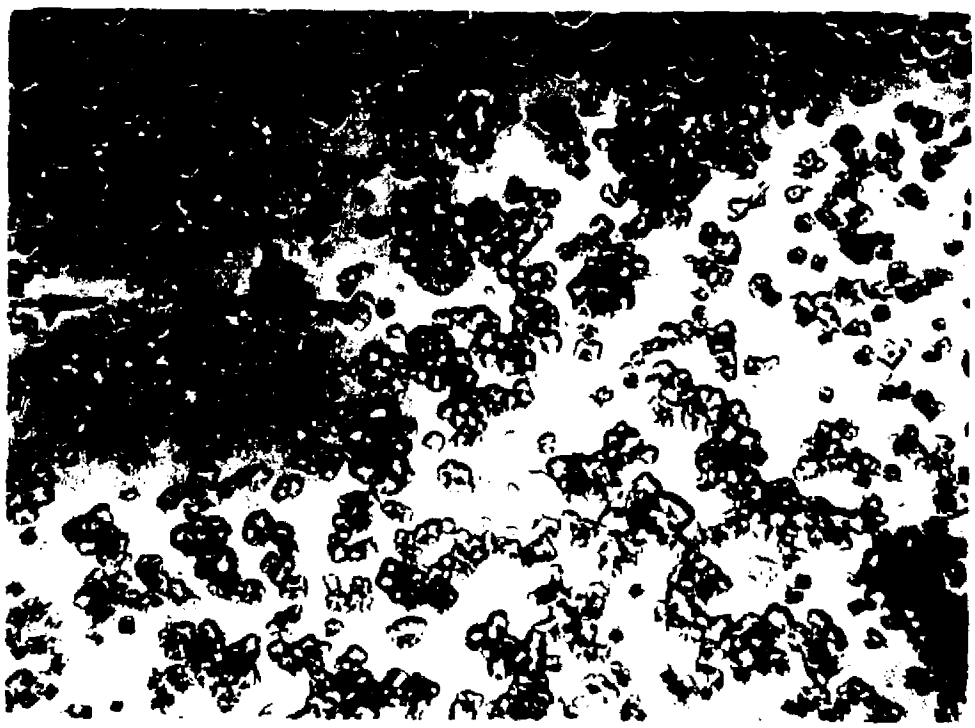

Fig. 5.6. Photomicrograph of calcium fluoride produced from homogeneous solution. (Straight transmitted light, 300x).

Fig. 5.7. Photomicrograph of calcium fluoride produced from homogeneous solution (500x).

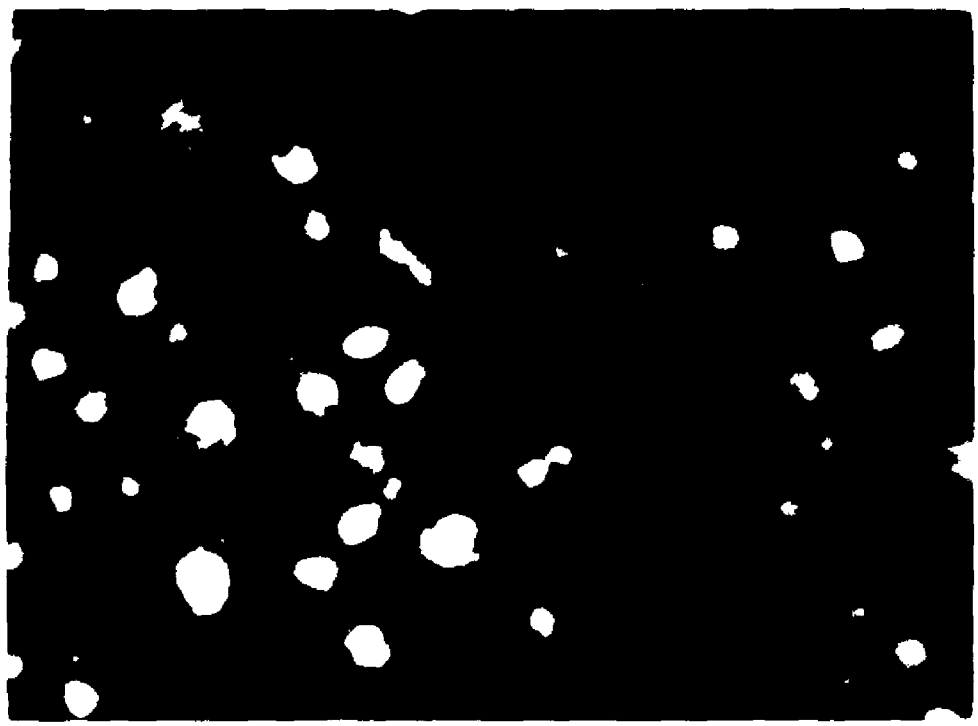

Fig. 5.8. Photomicrograph of calcium fluoride produced by Baker and Adamson (500x).

CHAPTER VI

DISCUSSION OF RESULTS, CONCLUSIONS AND EXTENSIONS TO THE PROBLEM

A. DISCUSSION OF RESULTS

From the preliminary studies summarized in Chapter IV, it was evident that in order for the precipitation of calcium to have any practical analytical importance, such detrimental characteristics, as colloidal formation, creeping tendency, gelatinous nature, and small particle size, etc., associated with calcium fluoride had to be overcome or sufficiently diminished.

Because calcium fluoride is the salt of a weak acid, it was expected that the final acidity of the solution would be a significant factor with respect to the attainment of quantitative results. This relationship is illustrated in Table II. Low results were obtained at pH values below 4.6 owing to the solubility of the calcium fluoride. At pH values of 4.6 - 6.1, the results obtained are within the normal experimental error allowed with gravimetric procedures, i.e., 0.30%. The final

pH used in most determinations discussed here was 5.7 ±0.1.

Table III indicates that best results were obtained if the precipitate was allowed to stand for three hours or more following the hydrolysis time before being filtered. This waiting period perhaps was necessary so that some of the smaller particles produced had a chance to grow into larger ones or be adsorbed on the surfaces of such crystals. Either Whatman #44 or Munktells No.00H filter paper was satisfactory for the filtration; however, most of the work was carried out using Whatman paper.

In the presence of large excesses of fluoboric acid, the resulting precipitate was amorphous (Fig. 5.1) and greater in weight than would be expected if only calcium fluoride were formed. Diaquo-calcium fluoborate, $[Ca(H_2O)_2][BF_4]_2$, may possibly be formed in such instances. According to Berzelius (3), hot water dissolves the acidic component of calcium fluoborate and leaves a residue of a basic salt containing an excess of calcium fluoride. Thus, perhaps what takes place may be formulated as

$$[Ca(H_2O)_2][BF_4]_2 \longrightarrow HF + [Ca(H_2O)OH][BF_4 \cdot BF_3] + [Ca(OH)_2][BF_3] + CaF_2 \qquad (6.1)$$

However, at temperatures between 300 and 500°C., calcium fluoborate dissociates into boron trifluoride and calcium fluoride. This indicates that heating the fluoborate of calcium at 800°C. should leave only calcium fluoride behind since boron trifluoride would be volatilized. The results obtained do not agree with this explanation. The increased weights may be explained, however, if the formation of borates of calcium is postulated. These compounds are quite stable at temperatures just above 1000°C.

Sixty per cent perchloric acid was found to remove the interference of the fluoride ion in the atomic absorption readings for calcium. This interference arises because of the formation of calcium fluoride which does not dissociate to yield the necessary calcium atoms. The presence of a strong acid such as perchloric in the solution insures the presence of calcium ions which are easily atomized as they travel through the burner. Why 60% $HClO_4$ should give the desired results and other concentrations yield enchanced values was not clear.

The precipitation of magnesium and lead fluoride in all concentrations studied led to high results as evidenced by Tables VII and VIII. Concentrations of 0.04g. and 0.05g. of

barium and sodium, respectively, could be present with 0.2g. of calcium and still yield good results (Tables IX and X).

The results obtained with the recommended procedure (Tables XI - XIII) were all within the accuracy desired in a gravimetric method. Table XIV confirmed the amount of calcium present in the precipitate by the values obtained when calcium fluoride was converted to calcium sulfate.

B. CONCLUSIONS

The results obtained by the method described here for the precipitation of calcium as the fluoride indicates that the method is suitable as a means of analysis for this important alkaline earth metal. In the concentration ranges studied (0.1 - 0.25g.), the results obtained were within the allowable limits of 0.30% error.

Although the precipitation of calcium fluoride has been used as a gravimetric method for the determination of fluoride, this seems to be the first time that the same method has been used successfully for the determination of calcium. Those who have prepared calcium fluoride in the laboratory state that the precipitate is very gelatinous, difficult to filter, and apt to become colloidal. Others (35) say that

the precipitate is slimy and when being filtered clogs up the filter paper to such an extent that it is almost impossible to complete the filtration. The precipitate obtained in this study was crystalline, (Figs. 55 - 57), easy to filter, and was neither gelatinous nor colloidal.

As a means for the determination of calcium, this method offers advantages over the classical oxalate procedure. First of all, as much as 0.04g. of barium can be present with 0.2g. of calcium and not interfere with the initial precipitation of the latter. In the case of the oxalate method, however, such small quantities of barium as 0.003g. require that the calcium be reprecipitated at least once again in order that this interference be removed (21). Furthermore, the presence of fluoride ions will not affect the results as would be the case with the oxalate method. Oxalate ions, of course, would not serve as an analogous interference when precipitating calcium fluoride. The fluoride precipitate, moreover, is not hygroscopic, need not have rigid ignition temperature control (Duval gives an ignition range of 400°C. - 946°C.), and need not be converted into another weighing form.

The interferences studied here were those that would be expected to be critical in both the oxalate and fluoride

methods. Work done by Kolthoff and Sandell (23) shows that sodium when present in amounts of 0.7g. will be coprecipitated with 0.1g. calcium to the extent of up to 13 mg as the oxalate. In this case also, sodium gives slightly high results when present in quantities of 0.1g per 0.2g calcium (Table X). Magnesium and lead interfere in both methods; however, the former can be tolerated in the oxalate method if present in small quantities. There is no apparent complexation phenomenom or supersaturated state to allow for even small quantities of magnesium to be tolerated when precipitating calcium as the fluoride. Ammonium, chloride, and nitrate ions do not interfere with the fluoride method as evidenced by the fact that these were present in the form of buffering agents in substantial amounts. Iron, aluminum and other trivalent ions which would normally be found with calcium, could probably be tolerated in greater amounts than with the oxalate method, since they form quite stable fluoro complexes.

The main reactions involved in the precipitation of calcium fluoride can be summarized as:

a) $CO(NH_2)_2 + H_2O = CO_2 + NH_3$

b) $BF_4^- + H_2O = BF_3(OH^-) + HF$

c) $2HF + Ca^{++} = \underline{CaF_2} + 2H^+$

C. EXTENSIONS TO THE PROBLEM

Analytical methods very often depend on compensating errors. Thus, an incomplete precipitation may be compensated by the coprecipitation of an impurity. For the work discussed here, it would be useful to determine the distribution coefficient and see if the precipitation of calcium fluoride is truly quantitative. If the value of λ were found to be 3.2×10^{-4} or less, then the precipitation could be considered so (18).

Another point for further study would be to investigate if both lead and barium can be more effectively excluded from the calcium fluoride by controlling the pH of the solution as well as the precipitant concentration.

The interferences considered in this study were those which were expected to be troublesome. Further studies on interferences should be made and include such species as Fe^{+3}, Al^{+3}, K^+, $H_2PO_4^-$, $SO_4^=$, etc. Such species as Fe^{+3} and Al^{+3}, however, should not cause serious difficulties because of their complexing capacities with the fluoride anion.

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VITA

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Major Field: Chemistry

Title of Thesis: A Study on the Precipitation of Calcium as Calcium Fluoride

Approved:

Philip W. West
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

W. C. Troy

H. M. Edwards

Dean

V. P. Guinger

Date of Examination: November 11, 1965